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Influence of Temperature and Composition on some Physical Properties of Milk and Milk Concentrates

IV. Thermal Expansion

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Einfluß der Temperatur und Zusammenhang einiger physikalischer Eigenschaften von Milch und Milchkonzentraten. IV. Thermische Ausdehnung

Zusammenfassung. Bei Anwendung der Dilatometrie wurden Messungen der scheinbaren thermischen Ausdehnung bei 11 Milcharten im Temperaturbereich von 0°—80°C durchgeführt. Die 11 Proben wurden in 3 Serien gruppiert, und zwar nach dem Verhältnis ihres Fettgehaltes zu ihrem Gehalt an fettfreier Trockenmasse. Es werden analytische Ausdrücke für die Beziehungen zwischen den termischen Ausdehnungskoeffizienten der Milch und ihrer Zusammensetzung bzw. Temperatur angegeben. Mit Hilfe dieser Ausdrücke ist das termische Verhalten der Proben mit einer Präzision von 1% vorauszusagen. Es wird auch ein Nomogramm wiedergegeben, aus dem die integrale relative Ausdehnung mittels der Temperatur, der Gesamttrockenmasse und des Verhältnisses von Fett- zu fettfreier Trockenmasse-Gehalt direkt abgeleitet werden kann.

Summary. Apparent thermal expansion measurements were carried out by dilatometry on eleven types of milk, grouped in three sets according to their fat to solids-not-fat ratio, over the temperature range of 0° to 80°C. Analytical expressions relating milk thermal expansion coefficients with its composition and temperature are given. These expressions predicted the thermal behaviour of samples usually within 1%. A nomogram is also presented for the direct derivation of relative integral dilatations from temperature, total solids content and fat to solids-no-fat ratio of the sample.

Introduction

Detection of watering and quality payment schemes have encouraged the density or specific gravity determinations on liquid milk. Studies have been also made on density changes associated with milk processing, i. e., whether pasteurization, sterilization or homogenization alter the density value of raw milk [1, 2], or in relation to water elimination in milk concentrating.

In spite of the above, the effect of temperature on the volume of milk remains almost unexplored over wide ranges of temperature and composition. Recently, however, Verma and Garg [3] have determined volume increases on skimmed milk and cows' milk over the 4°—95°C range and computed average expansion coefficients; Rambke and Konrad [4] have studied, on their part, the behaviour of different types of milk between 5° and 80°C and reported density-dry matter equations.

The present work deals with the determination of thermal expansion on different types of milk, at several concentration levels and over a wide range of temperature, 0°—80°C, with the major aim of formulating analytical expressions of practical use as far as dairy products technology is concerned.

Experimental

The dilatometers, volumetric type, built in Pyrex glass consisted of an approx. 7-ml bulb and a capillary of 1 mm ∅ and 40 cm of graduated scale. The bulb was previously gauged, the capillary calibrated and the dilatometer performance verified by measuring distilled water.

Mercury was used as confining liquid and proper correction was made; glass expansion correction was also carried out by taking 10^{-5}/deg C as an average cubic expansion coefficient for Pyrex glass. Dilatometers were totally immersed in the thermostatted liquid to avoid errors due to emergent stem. A thermostatic bath provided with auxiliary equipment to allow work below room temperature and a viewing port was used, the temperature control being better than ± 0.05°C.

In order to standardize experimental conditions, the samples were submitted to the treatments reported in previous cases [5, 6, 7], where other properties were dealt with. The characteristics of the samples are shown in table 1.

Table 1. Composition of Samples (N = 5 in each category)

Milk	Series	Concentration grade	Fat content (f), % Mean	Fat content (f), % Range	Total solids (s), % Mean	Total solids (s), % Range	Nitrogen, % Mean
Skimmed milk	S	1	0.12	0.07— 0.17	8.18	8.14— 8.26	0.45
		2	0.18	0.17— 0.19	16.62	16.30—16.98	0.91
		3.5	0.35	0.32— 0.37	28.31	28.01—28.56	1.50
Half and half milk	H	1	1.56	1.50— 1.64	9.17	9.15— 9.22	0.44
		2	3.05	2.99— 3.15	18.53	17.77—18.93	0.90
		3.2	4.87	4.78— 5.10	29.07	28.59—29.64	1.40
Whole milk	W	1	3.05	3.01— 3.09	11.03	10.86—11.25	0.46
		1.5	4.58	4.50— 4.63	16.43	16.19—16.59	0.68
		2	6.00	5.97— 6.09	21.92	21.70—22.40	0.92
		2.5	7.28	7.21— 7.36	27.47	26.97—27.74	1.18
		3.6	10.51	10.37—10.71	39.57	38.55—40.56	1.65

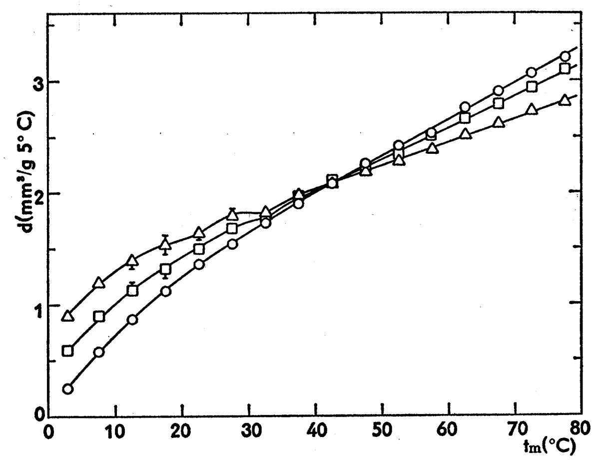

Fig. 1. Range and mean value of apparent differential thermal expansion determinations on skimmed milks as a function of temperature. o, S-1; □, S-2; △, S-3.5

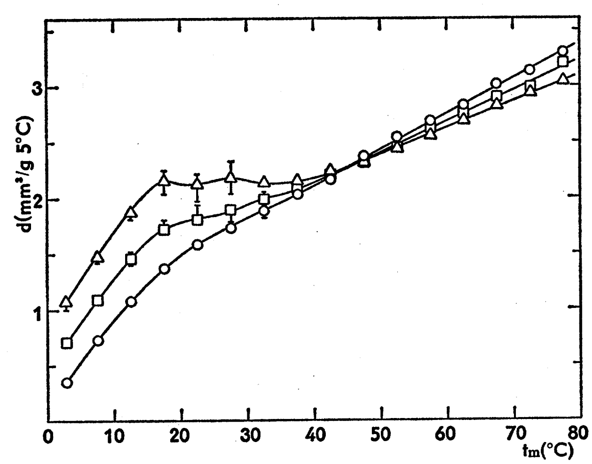

Fig. 2. Range and mean value of apparent differential thermal expansion determinations on half-and-half milks as a function of temperature. o, H-1; □, H-2; △, H-3.2

Results and Discussion

Measurements were made by 5°C steps and apparent differential expansions (mean values from 5 samples in each milk type) against mean values of the corresponding temperature increments are graphically represented in figures 1, 2 and 3 for skimmed milk, half-and-half and whole milk series, respectively.

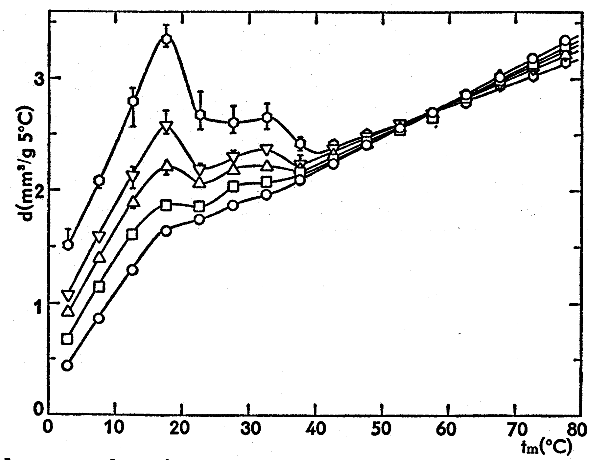

Fig. 3. Range and mean value of apparent differential thermal expansion determinations on whole milks as a function of temperature. o, W-1; □, W-1.5; △, W-2; ▽, W-2.5; ○, W-3.6

All the curves presented the same pattern and, obviously, strongly resembled heat capacity-temperature profiles [5]. So that a melting zone of medium-melting glycerides with a maximum between 15°C and 20°C and a smaller one of high-melting glycerides with a maximum at about 30–35°C were observed, melting expansions being larger as the fat content increased. Final melting of the fat phase was, likewise, at about 40°C, thus pure thermal expansion was only recorded at higher temperatures. But the curious finding of this work was that every set of milk exhibited a temperature where each milk of the set observed the same thermal expansion value, i. e., 42.5°C and 2.1 mm³/g 5°C for skimmed milks set; 45 and 2.3 respectively for half-and-half milks set; and 57.5 and 2.7 respectively for whole milks set, approximately.

Table 2. Relationships between thermal expansion and temperature in the range of 40° to 80°C

Milk types	$d = a_0 + a_1 t_m$ a_0	mm³/g 5 deg C a_1	Corr. coef.	Std error*.
S-1	0.721	0.0322	0.9986	0.76
S-2	0.817	0.0285	0.9990	0.62
S-3.5	1.184	0.0211	0.9985	0.55
H-1	0.867	0.0314	0.9987	0.74
H-2	1.014	0.0278	0.9983	0.55
H-3.2	1.259	0.0229	0.9989	0.60
W-1	0.934	0.0309	0.9997	0.46
W-1.5	1.033	0.0290	0.9976	1.01
W-2	1.121	0.0276	0.9991	0.62
W-2.5	1.285	0.0249	0.9981	0.67
W-3.6	1.472	0.0215	0.9980	0.68

* Standard error, as per cent, calculated by $100 \left[\Sigma \left(\frac{\text{exp-cal}}{\text{exp}}\right)^2 \Big/ n\right]^{1/2}$ where n = 8

Thermal expansion exhibited a reduz linear dependence with temperature that could be described by the equation,

$$d = a_0 + a_1 t_m \quad mm^3/g\ 5°C$$

where t_m is the mean temperature of the five-degrees increment. The regression analysis gave the values shown in table 2 for a_0 and a_1 parameters.

Table 3. Concentration effects on thermal expansion over the 40—80°C range

Milk set	$d = a_0 + a_1 s + (a_2 + a_3 s)\ t_m$ mm³/g 5degC				
	a_0	a_1	a_2	a_3	Std. error
S	0.514	0.0232	0.0371	—0.00056	0.76*
H	0.665	0.0204	0.0355	—0.00051	0.72*
W	0.720	0.0192	0.0345	—0.00033	0.70**

* As defined in table 2 and n = 24
** n = 40

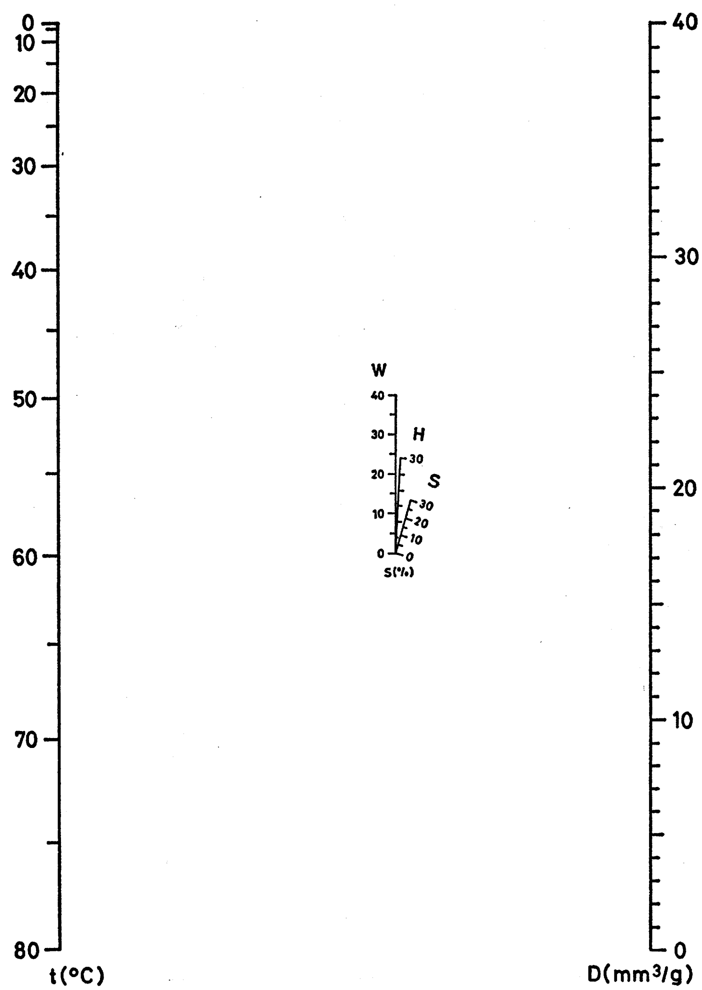

Fig. 4. Nomogram for the derivation of relative integral expansions on the 0° to 80°C temperature interval ($D_0 = 0$) from temperature and total solids content, by the straight-edge method. Edges marked S, H, W refer to total solids contents of skimmed, half-and-half, and whole milks, respectively

Calculated values of d in accordance with that are graphically represented by straight lines in figures 1, 2 and 3; standard errors refered to the eight mean thermal expansion values in each category were usually lower than 0.7%.

Concentration effects could be expressed by means of the following equation,

$$d = a_0 + a_1 s + (a_2 + a_3 s)\, t_m \quad mm^3/g\ 5°C$$

where s is the percentage total solids content and the parameters a_i, function of the type of milk, obtained the values given in table 3.

The behaviour of the three sets of milks, however, could be expressed by a single equation, thus the following one was found to yield thermal expansion coefficient calculations with an absolute standard error of ± 0.02 for any milk,

$$d = 0.104 + 0.120r + (0.0046 - 0.0023r)\, s + [0.0074 - 0.0015\, r - (0.00011 - 0.00013\, r)\, s]\, t_m \quad mm^3/g\ °C$$

t_m is now the mean temperature of one degree increment and r is the fat to solids-not-fat ratio of the sample, a characteristic value of each set.

Relative integral expansions may be readily calculated by integrating any of the expressions given before but, in order to cover all the temperature range explored, total expansion data were also treated by least-squares procedure and, assuming zero value at zero degrees, the following quadratic in t equation was obtained.

$$D = \{[23.3 + (6.71 + 12.80r)s]t + [4.43 - (0.071 + 0.064r)s]t^2\} \times 10^{-3} \quad mm^3/g$$

which applied for any milk on all of the temperature range from 0° to 80°C and fitted experimental results with an standard error (n = 171) of ± 0.40 mm^3/g.

For a rapid derivation of relative integral expansions this equation was converted into graphical form in the nomogram of figure 4, this consisting of two vertical (t and D) and one diagonal (s) edges. By pivoting on the required s value and crossing the t axis through the selected temperature, an straight-edge intersects the D axis yielding the estimation figure for the total expansion of the sample.

Some loss of accuracy took place in the construction of the nomogram, this being particularly noticeable at temperatures where butter fat melts. Consequently, estimated values of D were less accurate at temperatures from 40°C downwards than upwards; accuracy also decreased as values for r increased and, within each set of milks, when concentration level increased. It was found to fit experimental data with a standard error of ± 2.22 mm^3/g.

Acknowledgement. This work is a partial fulfilment of the research project UR-E25-(60)-37 financed in part by a grant made by the U.S. Department of Agriculture under P.L. 480.

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